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Introduction.

In determining the global methane budget the sources of methane must be balanced with the sinks and atmospheric inventory. The approximate contribution of the different methane sources to the budget has been establish showing the major terrestrial inputs as rice, wetlands, bogs, fens, and tundra (Matthews and Fung, 1987; Stevens and Engelkemeir, 1988; Cicerone and Oremland, 1988; Wahlen et al., 1089; Fung et al., 1991). Measurements and modeling of production in these sources suggest that temperature, water table height and saturation along with substratum composition are important in controlling methane production and emission (Tyler et al., 1986, 1987, 1997; Crill et al., 1988; Moore and Knowles, 1990; Cicerone et al., 1992; Moore and Roulet, 1993; Yavitt et al., 1993; Moore et al., 1994; Tyler et al., 1994; Baubier et al., 1995; Moosavi et al., 1996; Granberg et al., 1997).

The isotopic budget of ^{13}C and D/H in methane can be used as a tool to clarify the global budget. This approach has achieved success at constraining the inputs (Stevens and Rust, 1982; Wahlen et al., 1989, 1990; Wahlen, 1993; Quay et al, 1988, 1991; Lowe et al., 1994). Studies using the isotopic approach place constraints on global methane production from different sources. Also, the relation between the two biogenic production pathways, acetate fermentation and CO_2 reduction, and the effect of substratum composition can be made using isotope measurements (Whiticar et al., 1986; Burke et al., 1988, 1992; Martens et al., 1992). Figure 1 (from Wahlen, 1993) shows the relation between the different biogenic, thermogenic and anthropogenic sources of methane as a function of the carbon and hydrogen isotope values for each source and the atmosphere, tropospheric composition. Included on figure 1 are the theoretical limits on the acetate fermentation and CO_2 reduction pathway reactions which constrain the biogenic inputs (Whiticar et al., 1986).

Methane emissions from ponds and fens are a significant source in the methane budget of the boreal region. An initial study in 1993 and 1994 on the isotopic composition of this methane source and the isotopic composition in relation to oxidation of methane at the sediment surface of the ponds or fen was conducted as part of our BOREAS project. The isotopic composition of methane emitted by saturated anoxic sediment is dependent on the sediment composition and geochemistry, but will be influenced by in situ oxidation, in part, a function of rooted plant activity. The influence of oxidation mediated by rooted plant activities on the isotopic composition of methane is not well known and will depend on the plant type, sediment temperature, and numerous other variables. Information on this isotopic composition is important in both understanding the bio-geochemistry of the system and also in determining the regional and global inputs for the methane isotope budget.

In determining the destruction of methane for balancing the atmospheric methane budget soil oxidation must be considered. The primary destruction rate for methane and isotope fractionation by OH in the troposphere have been estimated by experiments and budget constraints and models (Davidson et al., 1987; Cantrell et al, 1990; Vaghjiani and Ravishankara, 1991) and by direct measurements in the lower stratosphere (Wahlen et al., 1990; Brenninkmeijer et al., 1995) but the rates or even reaction mechanisms are still uncertain. In addition to OH destruction there is a small but significant net consumption of atmospheric methane by moist aerobic soils (Keller et al., 1983, 1986, 1990; Whalen and Reeburgh, 1990; Crill, 1991; Striegl et al., 1992; Deck et al., 1993). The exact quantification of this consumption in the global budget is not well known but it could be from 5% to as high as 15% (Born et al., 1990; Crutzen, 1995) and has been found to be sensitive to the climate influenced parameters of temperature and moisture (Mosier et al., 1991; Tate and Striegl, 1993; Mosier et al., 1993; Bender and Conrad, 1994; Czepiel et al., 1995; Castro et al., 1995; Ball et al., 1997). Isotopic changes in methane associated with soil oxidation has been investigated in very few cases (King et al., 1989; Deck et al., 1993; Tyler et al., 1994a), and a fractionation value for ^{13}C (or more importantly D/H) to be applied to the global soil uptake is uncertain.

Con-current consumption of methane in association with anaerobic production has been recognized in virtually all areas where substantial methane fluxes have been measured. In regions of high methane production such as tundra, bogs and fens, consumption in surface layers can be a direct regulator of methane emission (Chanton et al., 1992, 1992a; Fechner and Hemond, 1992; Kelly et al., 1992; Happell et al., 1993; Bergmaschi and Harris, 1995; Granberg et al., 1997). Methane oxidation balanced with consumption at a high rate is associated with rice paddy methane production (Sass et al., 1992; Tyler et al., 1997). In drier aerobic zones of tundra, bogs and fens, in close spatial proximity with the anaerobic production, net methane consumption at ambient air methane levels is found (Whalen and Reeburgh, 1990; Moosavi et al., 1996). In extensive areas with moist soils including sub arctic, boreal forest, temperate forests and grasslands, tropical forests and savanna, and even desert soils, minimal net consumption of methane is often observed close to sites of production. It has been suggested by Reeburgh, 199X that when gross methane consumption is compared to gross production from all areas, that the consumption is a significant fraction of the production term and that global budgets should be described to reflect this. Incubation experiments on wetland soils (Moore and Knowles., 1990; Moore et al., 1994) show the ability of the soils to support production or oxidation depending on oxygen levels. The work of Bender and Conrad, (1994) suggest that two different species of methanotrophs exist. One species, primarily, in association with methanogens in a production /consumption relationship with the ability to utilize methane at higher than ambient concentrations, and another species which is able to utilize methane at ambient and sub-ambient methane concentrations. Consumption of methane in soils appears to be sensitive to temperature, moisture content and nutrients (N- fertilization) (Mosier et al., 1993; Czepiel et al., 1995; Castro et al, 1995), but the greater control on consumption appears to be the soil structure with respect to porosity and channeling which determine the diffusional transport of air in the soil (Striegl et al., 1992; Bender and Conrad, 1994; Ball et al., 1997) and the distribution of the bacteria in the soil (Koschorreck and Conrad, 1993). Studies in both tropical and temperate regions show a marked change in methane consumption when forest soils are cleared, or savanna and grassland are converted to pasture or cultivated (Keller et al., 1990; Poth et al., 1995).

Studies of the isotopic fractionation in methane during soil consumption are few and the error in individual analysis often large. Data from boreal soils (King et al., 1989), boreal forests (Deck, in preparation), temperate and tropical soils (Tyler et al., 1994a; Deck et al., 1993) and even landfill soils (Bergmaschi and Harris, 1995) show a range of isotope fractionation factors (Table 1). This range is, however, consistent with the observations of Coleman et al., (1981) on methane oxidation by methanotropic cultures in the laboratory which showed fractionation factors $\alpha = 0.975$ to 0.987. For soil methane oxidation values to be incorporated into the global methane budget, a better understanding of the controls on the observed fractionation must be determined. Allowing the assignment of soil oxidation values for different regional soils based on measured values would require an extensive set of measurements. A more desirable approach would be to determine the environmental controls on the apparent soil isotope fractionation. The BOREAS sites provided a selection of sites representative of a large global extent where the consumption of methane by soils could be estimate using the isotopic approach.

Results of previous soil methane isotope consumption studies.

The recent work by our group prior to, and in preparation for the NASA, BOREAS provided a set of data which can be used to evaluate methane oxidation and carbon isotopic fractionation in boreal forest soils. This information on dry soils (Deck et al., 1993) and a moist temperate forest site can be compared to the other available studies. For procedural comparison, our samples for all sites except the forest site in Albany, NY were sampled in 2 liter glass flasks from, small, approximately 0.5 m^3 volume, chamber enclosures with the actual methane concentration being determined on the sample prior to isotopic analysis. Chambers were mixed before sampling and were not open to the air during the time required to fill the sample. Samples for the BOREAS work in 1996 were taken at 1 hr and duplicate samples at 2 hr and the difference in concentration found between the replicates was rarely greater than 1%. We have, thus, not corrected our results for air dilution during sampling.

A moist forest site near Albany, NY was measured in the summer of 1989 and 1990. This site had a very porous, organic rich, soil where sites of measured methane consumption in excess of 5 $mg/m^2/d$ were within meters of, water saturated, methane producing sites. A set of large volume samples, taken within 2.5 hr of enclosure using a large (aprox. 4 m^3) plastic tarp chamber, were analyzed at high precision. The results and derived enrichment coefficient α of 0.983 for this data are shown on figure 2, where $\alpha = \{\ln[(\delta^{13}C_t+1000)/\ \delta^{13}C_o+1000)]/\ln(f)\}+1$, for initial (o) and time (t) isotope concentrations and a (methane concentration determined) fraction remaining (f). (King et al., 1989).

In 1992 and 1993 a dry forest site (Los Monos Canyon Reserve) near Vista, CA was sampled approximately monthly. Several sites of open forest and grassy areas were sampled where a compact soil character of low organic content was common. The average moisture content of the Los Monos soil during the summer and fall sampling times was low, 2% w/w or below, and methane consumption rarely exceeded 0.8 $mg/m^2/d$ even though soil methane profiles showed rapid concentration decreases from the surface to 40 cm. In the winter and spring, following rain events, the soil moisture increased and methane consumption rates as high as 2 $mg/m^2/d$ were observed. Although the chamber size (large volume to soil area ratio), low consumption of methane, and analytical procedures introduced uncertainty into the data, the results (Figure 2) show the effect of fractionation with decrease in methane and suggest an observed fractionation of approximately $\alpha = 0.978$ significantly greater than that found for the temperate, Albany, forest site. Chamber enclosure time for these experiments were kept to < 3 hr despite the low methane consumption.

Experimental approach and summary of the BOREAS sampling.

Methane isotopic measurement in conjunction with the BOREAS project were made on sample taken during the field efforts in 1993, 1994 and 1996:

Sediment methane production

Ponds and fens often show visible bubble release of gasses and have large net fluxs of methane into the atmosphere. The investigations started here were not meant to quantify the net flux, but to allow a determination of the isotopic composition of the emitted methane. Dislodged bubbles from anoxic sediments from 5 beaver ponds and the NSA Tower Fen site were sampled in 1993. Funnels at the water surface quantified bubble release while monitoring of the overlying water and sediment pore waters was made to determine sediment/water gas exchange. Bubble and sediment/water samples from the Tower Beaver Pond (NSA, TBP) were taken in 1994 to determine the carbon and hydrogen isotope values of methane emitted from this site. Initially it was anticipated that work on these samples and work on sediment production would continue thorough out the project, however, with the imposed budget cuts and recommendations by the science team, limited sampling was made. Also, as a result of the lack of collaboration with other investigators supporting data for the samples is incomplete and few conclusions can be made from the results obtained. The data is presented as appendix 1 however, with a brief description of the results.

Forest soil oxidation

To determine the effect production and oxidation at the land surface has on the overlying atmospheric concentration the flux of any gas through the various pathways into or out of the soil or sediment by biota must be determined. In the case of methane in boreal forests, the interaction between the atmosphere and forest soils is direct and not thought to be mediated to any major extent by trees or woody plants. Thus, the flux of methane into or out of the soil can be determined, and the isotopic fractionation examined, by placing closed chambers on the surface for a period of time. In addition, samples of soil gas taken below the soil surface will provide information on the rate of methane consumption and the isotopic fractionation with soil depth. In either situation changes in concentration and isotopic composition of methane over time will indicate the effect the soil or sediment will have on the overlying atmosphere (source/sink).

The basic problem with this sampling approach is to avoid having chamber placement cause perturbations of the naturally occurring gas exchange either through biological or physical changes in the system. To this end, the temperature, humidity, air circulation, light and other parameters inside the chamber can be controlled to mimic those outside the chamber. In many cases controls on chamber parameters are not adequate for extended periods of time and the best sampling strategy is to leave the chambers enclosed for only the time required for the minimum consumption of methane necessary to ensure the accuracy needed in the determinations. For concentration changes in methane, the high degree of precision attainable allows for short (0.3-0.5 hr) maximum enclosure times. In the determination of isotopic methane composition the times necessary for measurable changes to be determined with reasonable precision in the analysis are a factor of 2 to 4 longer. In addition, care must be observed at all times to ensure that the sampling and storage procedures do not introduce additional errors. Finally, it must be realized that chamber, and soil probe samples, and/or any discreet measurements at a finite number of sites can only approximate the estimates of actual average soil-atmosphere interaction, at any one site.

Gas samples from flux enclosures (chambers) over the soil and subsurface soil gas samples were taken and returned to our lab for analysis. While some concentration measurements were made in the field in conjunction with others investigators, our data sets consists of methane concentration and carbon isotope ($^{13}C/^{12}C$) ratios for each analyzed sample. Due to the large amount of time necessary for the processing of the isotope samples, a limit on the number of samples taken in any field season was necessary. The fewer the number of samples or the greater variability in site characteristics, the poorer the data approximation. The limitations on number of samples taken imposed by isotopic analysis procedures are significant in this study, but are balanced in part by the uniformity in microbial biochemistry which drives the methane production and consumption in all areas.

Sampling data and sites

Data were collected once in 1994 and at four time periods in 1996, from two sites near the towers at the Old Jack Pine (OJP) and Young Jack Pine (YJP) sites, in the Northern Study Area (NSA). A set of chamber measurements from the SSA, OJP and YJP sites along with soil gas samples were also obtained in 1994. At OJP the Crill (TGB-1) Lichen chamber #4 and the Crill Moss chamber #7 were sampled. For the YJP Moore (TGB-5) chambers, #4 and #6 were sampled. Two liter samples were taken from each of the chambers, drawn over a 1 to 3 min sampling period, at times of 0.75 to 7 hr depending on estimated methane uptake. The chambers at the OJP were approximately 20m apart while those of the YJP were within 5m of each other . Soil probe samples were taken at shallow depths in the immediate (1m) vicinity of the chambers. Samples were drawn slowly (5 min for 2 liters) to avoid contamination from gas sucked in from intermediate levels. A summary description of the sampling follows:

Sampling NSA93 24-Aug-93: Bubbles from dislodgment, Fen Tower ramps 1, 2 and 3. 25-Aug-93: Bubbles, Gilliam Rd. Beaver Pond (GBP, 14.5 km N of 391) west shore. 26-Aug-93: Bubbles, OBS beaver ponds #3, 4, and 1, Tower Beaver Pond (TBP) south shore. All samples were from near shore water at depths of 10-50cm; abundance and species of plants and algal varied growth.

Sampling SSA94 4-Aug-94: YJP TF-4 chambers A, B, and D soil probes A/B 15cm, 20cm. OJP ,TF-4 chambers G, H, and J probes G/H 15cm, 20cm. Samples taken by the R. Striegl TF-4 group, chamber collection times were long (14-16 hr.).

Sampling NSA94 24-Aug-94: OJP, three chambers at TGB-1 lichen site, no collars, three soil gas probes. YJP, 3 chambers TGB-3 collars #4, 5 and 6, five soil probes 1-2 meters south of TBG-3 soil tubes. 25-Aug-94: Tower beaver pond samples collected from funnels, pizometers, overlying water profiles. BOREAS AES 2ppm and 0.9ppm standards sampled. 26-Aug-94 YJP TGB-3 soil tubes site 1c and 3a sampled at 20 and 40cm depth. Ambient air sampled each day.

31-Aug-94 through 13-Sep-94: Tower beaver pond samples, gross bubbles, funnel, pizometer, and water samples. Taken by A. Dove TGB-3.

Sampling NSA96 29-May-96 to 3-Jun-96: Ground frozen below 15 cm of the surface: soil temperature < 10C; high degree of water saturation. One sample taken at each chamber, OJP at approximately 4.5 hrs, YJP at approximately 6 hrs. No soil probe samples.

28 and 29-Jun-96: One sample taken from each chamber at 1.5 to 2 hrs (sampled by Kathleen Savage TGB-3). No soil gas samples.

1-Aug-96 to 4-Aug-96: General surface temperatures approximately 25C; weather good and dry. Duplicate samples at 45 and 90 min after closure for both OJP chambers; 4 soil probe samples, two near each chamber at approximately 20 cm depth. Sampling for the YJP site was identical except for sampling times of 1 and 2 hrs for the chambers.

8-Sep-96 to 12-Sep-96: OJP sampled 8-Sep; light showers two days prior; chamber were sampled in duplicate at 1 and 2 hr times. Soil samples, two near each chamber at approximately 15 cm depth. Cold heavy rain for two days. OJP samples taken on 11-Sep, temperature <9C. Single samples at 1 hr, duplicate samples taken from each chamber at 2 hrs after closure. Two soil probe samples taken 15 and 17 cm. Two ambient air samples collected.

Experimental.

Samples from the wet areas,beaver ponds and fen, were taken from the shore or walkways. Samples taken for methane production from submerged sediments were primarily obtained by capturing bubbles that had either been released over time or were dislodged by motion from the surface of the sediment. The gas from these samples (20 to 100cc) was transferred to evacuated serum bottles with rubber septum caps. Several sets of samples equilibrated with helium gas from water samples taken above the sediments, or from pizometers in the sediments were also collected by the TGB-4 group.

Soil gas exchange (NSA) was measured using either aluminum (OJP) or plastic (YJP) enclosures of $0.4m^2$ and $0.075m^3$ or $0.05m^2$ and $0.018m^3$, respectively. The chambers rested on skirts permanently placed 10 cm deep in the soil in 1993 or 1994 and were equipped with a water seal to prevent air leakage. Once the chambers were in place the air was mixed approximately every 5 min either with a fan or by rapidly drawing and returning 50cc of air several times with a syringe. After a suitable time period (0.75 to 2hr, in most cases) air samples were withdrawn through a restricting manifold, to prevent a sudden vacuum in the chamber, into 2 liter evacuated glass flasks with high vacuum valves. The sampling manifold was evacuated to remove extra air and to check for leaks, after being attached to the sample flask, prior to the sample being taken. Sub surface gas samples were taken using a pointed 3/8" steel probe inside of which was a 1/8" tube connected to a nose chamber open to the soil through several small holes. This probe was pushed into the soil to the desired sampling depth, the manifold attached and evacuated, and then the sample flask (as above) was filled. For the sub surface samples the manifold was set to allow approximately 3 min for the flask to fill. For a few of the 1994 soil gas samples, horizontal 1/8" sample tubes (TGB-3) previously placed at several depths in the soil were used following the same procedures.

Methane concentration analyses were performed with a flame ionization gas chromatograph equipped with a 2m 1/8" Porapack Q (60-80 mesh) column using nitrogen as a carrier gas. Replicate peak height measurements from a chart recorder were used to quantify the results. The inlet line to the sample loop was equipped with a precision pressure gauge calibrated to 0.5%. Methane in air standards at 959, 1649, and 2722 ppb were run at several pressures, several times during sample analyses, to allow correction for any deviation in linearity as a function of pressure or concentration.

Separation and combustion of the methane in the chamber and soil gas samples to CO_2 for the mass spectrometric analysis was performed on an extraction line specifically designed for this type of sample. The 2 liter (air) sample was passed at 50cc/min or less through two LN_2 (liquid nitrogen) cooled traps to remove water, CO_2 and other condensable gases, then through a trap containing several grams of 10 mesh activated charcoal. This charcoal column retains 500-800cc of air (N_2, O_2) at any time with methane and other trace components totally retained. After the entire sample is processed (down to <10 torr), and pumped at vacuum for 15 min, the charcoal is allowed to warm from LN_2 temperature to approximately -150C over a period of 5 min. During this time the majority of the air retained on the charcoal is allowed to bleed off at a carefully controlled rate, while the methane is retained. Then the charcoal column is immersed in a -90C acetone bath and the air allowed to continue to bleed off at a controlled rate, again retaining the methane. A low flow of helium is passed through the column to dislodge additional air from the column for 1 min. At this time the gas on the charcoal is transferred to a smaller charcoal column (approx. 1 gm) in LN_2, by warming first to room temperature 10 min, then at 240C for 10 min. In a manner similar to that above, the second charcoal column is warmed and again any remaining excess air allowed to be removed. Helium is passed through the first column onto the second to maximize the transfer. At this stage 1 to 2 cc of total gas containing approximately 3.7 microliters (or less) of methane (corresponding to the methane in 2 liters of ambient air) remains. This sample is transferred to a inlet loop of a thermal conductivity gas chromatograph fitted with a special low flow MS5a column using helium carrier gas. The flow parameters of the column and detector have been adjusted so that a nearly complete separation of methane from nitrogen can be obtained with an elution time of 25 min at room temperature. The methane eluting from the column is captured on a short MS5a column and transferred, following removal of the residual helium, with a MS5a finger to the combustion system. The combustion of the methane was done by condensing the methane sample at LN_2 temperature onto 2 aluminum oxide pellets coated with platinum (Alfa #89106), condensing a tenfold excess of pure oxygen onto the pellet, followed by a combustion of the mixture at 650C for 1 hour. The CO_2 was then separated from the water produced trap at -70C, quantified, and then sealed in a 6mm glass break tube for later mass spectrometric analysis. Extensive work was necessary to initially clean, and learn how to keep the combustion pellets clean. This resulting in a low CO_2 blank for this step. Samples with methane concentration higher than ten ppm required proportionately smaller than 2 liter air samples for analysis. Samples in the percent methane range were able to be processed using similar GC steps and combustion. When more then 50 ul of water (as vapor by volume) were generated the water was saved for D/H isotope analysis.

Calibrations were performed using methane standard concentration determinations and isotopic analysis conducted at SIO during the lab analysis. Methane determination on field samples were made with a manometric manifold inlet loop on a flame ionization gas chromatography system with a 2 meter 1/8" 60-80 mesh Poropack Q column, nitrogen as carrier gas. Calibration was performed with a set of 5 working standards covering the range of 0.8 to 2.8 ppm previously calibrated against SIO/CSIRO international standards (R. Weiss) to better than 0.2%. Overall precision and accuracy of our system in this range was approximately 0.5%. Calibration against the BOREAS working methane standards (0.9 and 2.0 ppb) also showed this agreement within experimental errors. Samples with higher than 3 ppm methane concentration were diluted and/or injected at reduced pressure and calibrated against volumetric standards up to 100% methane. Uncertainty for these samples was approximately 5%.

For the 2 liter soil chamber and probe samples runs on the extraction line, pure nitrogen blank determinations, synthetic air standards and calibrated isotopic methane standards passed through the lines and combustion systems during development provided the calibration of the system. For calibration during normal runs clean SIO air was used as a standard, with a methane ^{13}C value of -47.2 permil PDB. Approximately 1 standard per 4 samples were run. Based on replicate SIO air standards (2 liters) and replicate 2 liter samples taken in the field the uncertainty in analysis was found to be primarily dependent on the uncertainty introduced in the separation procedure. This was determined to be approximately +/- 1 permil. The mass spectrometric determination error was far smaller than this value and is included in the +/- 1 permil value. Actual runs of the mass spectrometer using our working standard and cold finger (-43.40 +/- 0.05 permil), measured in the size range of the samples, yielded a running precision of better than +/- 0.1 permil.

For samples of higher methane concentration from production sites the variability for the sample size processed again limited the error to approximately +/- 2 permil (PDB) for carbon and +/- 5 permil (SMOW) for hydrogen isotopic composition.

Error in this data are a combination of errors introduced during sampling, sample transport and storage, processing and analyses. The greatest uncertainty in any of the data results from the synoptic nature of the discrete sampling. Samples taken in close proximity to each other varied in their data values, often with results differing by more than any combination of experimental errors would allow. In this study sample storage, processing and analysis procedures were checked before and during the field work using standards and blank determinations, and the associated error determined.

Errors introduced during sampling could be inferred from several conditions, such as lack of good seals on chambers, or long chamber deployments, which did not reproduce the normal planned conditions of sampling. Where there are indications that this happened, it has been noted with the sampling data. Analysis of some of the data, such as with the methane production samples show an enormous range of values, in part because they were sampled in several different ways, at several different sites. Also, questions such as dislodged bubbles representing the release of methane as shown by funnel collected bubbles are not considered. Lacking a more complete data set describing many additional parameters influencing methane production/consumption, analysis of even the error from this type of sample is difficult.

Results and Discussion.

The results of the BOREAS experiments as tabulated for the BOREAS documentation set are included in appendix 1 for the beaver pond and fen sites where methane production was studied, along with a short discussion. For the soil methane oxidation experiments, the results from chamber enclosures and soil gas samples are discussed here while the tabulated results are included as appendix 2.

In a modeled "ideal" case where soil methane consumption and soil parameters are uniform with depth and biological activity constant over time and independent of methane concentration, methane consumption in an enclosure placed on the soil surface will show a decrease in concentration in a linear fashion. Soil methane concentrations with depth should also be linear. In this ideal case a linear trends should be seen in isotopic values measured if plotted against the natural log of the fractional concentration remaining. In a sampling system of this type any leakage of the chamber with outside air, at the same initial ambient concentration and isotopic composition, will change the concentration and isotopic composition. Equally. A change in the isotopic composition vs concentration relationship if plotted as ln (f) will be seen as a departure from linearity.

To analyze the effect sampling might have on the data collected, the situation where a 20 liter chamber at 1400 ppb concentration having a 2 liter sample removed and replaced with ambient 1850 ppb concentration air was modeled. The modeled change in concentration in the chamber would be approximately 40 ppb with an isotopic change of -0.25 ‰ using ambient and sample values of -47.5‰ and -44.7‰ respectively. The change to the derived α from this modeled data would be -0.0001. With respect to our actual samples this is a worse case scenario since half the chambers sampled were of approximately 75 liter volume. For our samples, an examination of the data for the 1996 enclosures (appendix 2) where 8 sets of duplicate 2 liter samples were taken shows that changes in concentration as a result of sampling were usually smaller than 25 ppb and in all but one case were towards a lower concentration indicating that gas from the soil not outside air was being advected into the chamber. Since the relation of isotopic change vs concentration found in the soil is approximately that observed in the chamber (to be discussed below), the effect of sampling in this case on the chamber data would be extremely small.

In the "real" soil/biological system several factors modify the conditions described above. Biological consumption of methane has been shown not to be uniformly distributed in the soil but more often localized in sub surface zones (Amaral and Knowles, 1997). Neglecting temperature and moisture effects, bacterial consumption is dependent on concentration, and slows as concentration decreases, often becoming minimal at concentrations below 200 ppb. Soil structure is also not uniform and soil diffusive transfer has been found to be very important (Ball et al, 1997; Dorr et al., 1993). Greater diffusion and advection in the surface layers can also influence the chamber determinations if mixing in the chamber does not match that outside the chamber. All of these factors can cause non linear profiles to be observed in the chamber concentration measurements as a function of time. However, since the biological isotopic fractionation is not normally a function of methane consumption rate or mixing, the data from isotopic measurements as a function of ln (f) will remain linear. This feature is shown on figure 2 where the data from the temperate forest near Albany, N.Y. are plotted.

Factors which are thought to possibly alter the isotopic fractionation are temperature, moisture level, oxygen concentration and carbon substratum composition. The research in the BOREAS sites was proposed to examine these factors. The data from most chamber enclosure samples taken in 1994 and 1996 are presented as figure 3. The 1994 NSA-OJP samples were taken on a very windy day with poor enclosure seals. As a result, the values show little consumption and are very close to the ambient air values. Values from the 1994, NSA-YJP site plot on or below the α = .984 line and in comparison to the data on figure 2 lie in approximately the same range as the Los Monos, CA data. The conditions for this set of samples were a fairly warm and dry soil similar to that at the Los Monos site suggesting greater effect of fractionation under these conditions as compared to the Albany, NY samples, where the soils were cool and quite moist, or the BOREAS 1996 samples. The data from the 1994 SSA sites (OJP and YJP), plot in a zone indicating significantly less fractionation than any of the other data which is puzzling since soil conditions were reported to be similar to those for the NSA samples (Striegl, per. Com.). A closer examination of the sampling data revealed a very long enclosure times, a factor which will be discussed below.

In 1996 attempts were made to closely replicate timing and sampling procedures for the chambers in the NSA, OJP and YJP sites (two sites each). The results for the late June, August and September samplings are shown on figure 3 and 4. The results from the early June sampling are not plotted as two of the four data point had enormous scatter, most probably due to the very cold, saturated and/or frozen soil conditions. The high correlation of the 1996 data over the range of soil conditions represented at the two sites sampled, with respect to temperature and moisture changes found from June through September in an average year, strongly suggests that these effects are not important during most of the time the soils are consuming methane. This result is consistent with the observations of Savage et al. (1997).

In trying to explain the anomalous trend of the data from the 1994, SSA, the 1996 data were examined in closer detail. When the data is expanded and differentiated as a function of chamber enclosure time a distinct difference in correlation between the 45 to 60 min samples and the ones taken at 90 and 120 min. is found (figure 4). The difference between the sets cannot be explained by sampling or leakage artifacts as shown above and must result from changes in either the isotopic fractionation constant with time or possibly the effect of concurrent methane production in the soil.

The concept of concurrent methane production with aerobic soil microbial consumption is not new. In many tundra and moist soils sites with neutral or minimal consumption have been found close to sites of production. For dry soils however, the concept of minimal concurrent production in a aerobic soil has not been examined, nor has the probable effect on the apparent values of α found in the limited isotopic fractionation studies that have been made (table 1). King et. al., (1989) mentioned this possibility, but did not mention that this might be a possible reason for the difference between the results for the two chamber experiments they describe. Briefly, the two chambers they measured showed fractionation values α of 0.974 and 0.984. To be sure, the condition in the chambers were not the same with regards to soil type and temperature, but more importantly may have been the chamber enclosure times of 2 and 8 hr, respectively. If methane consumption over the enclosure time is a function of the available methane remaining while concurrent production a constant (or possibly) increases due to decreasing oxygen in the soil), the net result will be a leveling trend in chamber methane concentration vs. time and a decreasing apparent enrichment in isotopic value over enclosure time. This also would explain the difference in the 1994 SSA samples taken with 18-20 hr enclosure times to those of the other BOREAS samples. This argument would also aid in the explanation of the non linear trends in concentration within enclosures as a function of time which have been observed in many Los Monos and BOREAS experiments (Our data, Crill pers. Comm.).

For the BOREAS sites Amaral and Knowles, 1997 found that the highest rates of consumption were near the subsurface lower organic and upper mineral layers 6 to 10 cm from the surface and that under some conditions a potential for methane production existed even in aerobic core sections. Savage et al., 1997 reported sporadic chamber measurement with net methane production at the Jack Pine site in 1994. Unfortunately most concentration measurements have been aimed at determining methane fluxes and not at exploring this factor. The limited number of isotope measurements that have been, or could have been, taken from small chambers has normally prevented a clearer observation of the effect on isotopic composition if it exists. Unfortunately the possibility that there is a change in the fractionation of methane as a function of methane concentration can not be discounted (Tyler et al., 1994), although the results of King et al., (1989) suggest this remains constant. Also, the possibility that the changes in the concentrations of oxygen and CO_2, and other artifacts of long chamber times may change the fractionation constant value as well as the rate need to be examined in the future.

To correlate the consumption and isotopic fractionation observed in the chamber enclosures to the soil itself, a series of soil gas samples were taken at sites near the enclosures at various soil depths. Some difficulties were encountered in obtaining these samples especially at the NSA, OJP site where the large amount of moss or lichen along with litter debris made a definition of the soil surface ambiguous. Also, rocks at the OJP sites resulted in a relatively non-homogenous soil matrix. Since 2 liters of soil gas needed to be removed, multiple samples with depth could not be taken. It was necessary to move the probe approximately 0.5 m between samples, so any correlation to a vertical profile is lost. The samples taken in 1994 were selected from a larger and more diverse set of sites around the enclosures than in 1996, and also were taken at generally greater depths.

The data, which are presented as figures 5, 6 and 7, show the general trend of decreasing concentration and less negative (more enriched) isotopic composition which would be expected from methane consumption continuing with depth into the soil. On each of the data graphs the best fit linear correlation has been draw through the data. As seen in all of the graphs a considerable increase in scatter in the data is found in the deeper, lower concentration samples. Resent measurements made under a pine tree at Scripps Institution of Oceanography have shown extensive fractionation of the methane isotopes next to roots resulting in very enriched methane isotope values (Fessenden, pers. comm.) which may be a possible explanation for some of the scatter observed in the deeper samples.

In graphs 5 and 6 where methane concentration and isotopic composition are plotted as a function of depth in the soil the linear trend in the data can be extrapolated to the surface, zero soil depth. Applying a diffusional mixing model, the intercept indicates the overlying gas composition which would in this case be approximately 1920 ppb and -53 ‰ ^{13}C for the overlying air. This is a significant deviation from the measured ambient air values of approximately 1850 ppb and -48 ‰ ^{13}C.

Two possible reasons exist for the observed shift. First, the ambients measured may not be representative of the atmosphere directly above the soil for much of the day, i.e. during the night. It is possible that during the night methane production at sites close to the chambers influences the surface layer air concentration enough that the soil profiles are influenced. Second, con-current production of methane in the soil region near the surface is influencing the observed soil profile, resulting in an apparent higher and lighter methane concentration for the overlying air. Both of these hypothesis do have merit. Ambients right above the surface were not taken at night, however, tower measurements have not, to our knowledge, shown any support for this theory.

Concurrent methane production would support our soil observations, if the primary zone of consumption were in the top 10 cm as shown by Amaral and Knowles

(1997) and below that level concurrent production showed greater influence. Additional support for this theory is strengthened by examining the data in figure 7. If the linear correlation determined by the data is used to approximate a hypothetical "α", relating the observed concentration change in the soil to the isotopic fractionation as done for the enclosures, a value of "α" = 0.993 is found. This trend of lower enrichment in the isotopic composition with decreasing methane concentration is what would be expected with concurrent methane production in the soil. Also the isotopic value corresponding to a concentration of 1850 ppb is approximately -50.2 ‰, a value lighter than the expected ambient air but not nearly as high as the figure 6 intercept of -53‰ for ^{13}C vs depth. It is important to note the position of the four samples from the SSA in 1994 which suggest a difference in the isotopic fractionation consumption/ production relationship as compared to the NSA samples. Since most of the TGB groups efforts were in the NSA no real information on the characteristics of the soil is available for comparison and, with the few samples obtained from the SSA additional, conclusions for these sites can not be made.

Conclusions.

Methane consumption the BOREAS soils at the NSA, OJP and YJOP sites was studied and the isotopic fractionation associated with the microbial oxidation measured. The fractionation constant derived was found to be dependent on the length of sample enclosure placement. The data from enclosures in place for less than 90 min. provided a value α of 0.983. Values of α from the same enclosures at longer times and from enclosures sampled at times longer than 6 hours such as the 1994 SSA samples show significantly less fractionation (values of α closer to 1.0). A few samples taken in 1994 indicate that greater fractionation may take place at some times, possible under very warm and dry conditions similar to those found at the Los Monos, CA site. The chamber enclosure data and measurement of the profiles of concentration and isotopic change with depth in the soils suggest that concurrent methane production at marginal levels in the soil would be a possible explanation for the observations.

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Table 1.

Kinetic isotope values for carbon in methane during soil oxidation

		$\alpha = k_{13}/k_{12}$
Coleman et al., 1981.	Bacterial cultures 26° and 11.5°C	0.975 to 0.987 (1)
King et al., 1989.	Boreal soils 2hr, approx. 14°	0.974
	8hr, approx. 4°	0.984
Tyler et al., 1994.	Temperate forest observed	0.983
	corrected (max.) for dilution	0.978
Deck et al., 1993.	Temperate forest, Albany NY.	0.984
	Dry forest, Los Monos	0.978 ± 0.006
BOREAS	Boreal forest,	
	1996 July, Aug., Sept.,	0.988
	Aug. & Sept. 45-60min.	0.983
	" " 90-120min.	0.992
	1994 SSA 18-20 hr.	0.994
Bergmaschi and Harris 1995.	Landfill emitted methane	0.992(2)

1) Hydrogen isotope fractionation measured at α = 0.675 to 0.897

2) Methane concentrations in the 20 to 60% range. Hydrogen isotope fractionation measured at α= 0.956

Figure Captions.

Figure 1. The major sources of methane and the atmospheric values as a function of their carbon and hydrogen isotope composition. The lines represent theoretical boundaries for methane production by acetate fermentation and CO_2 reduction. Each box contains a substantial number of samples.

Figure 2. Soil methane isotope values determined in enclosures from the Albany, NY. Temperate forest and Los Monos, CA dry forest sites as a function of the natural log of the fraction of methane remaining. The line represents the fractionation factor (α) for the Albany samples.

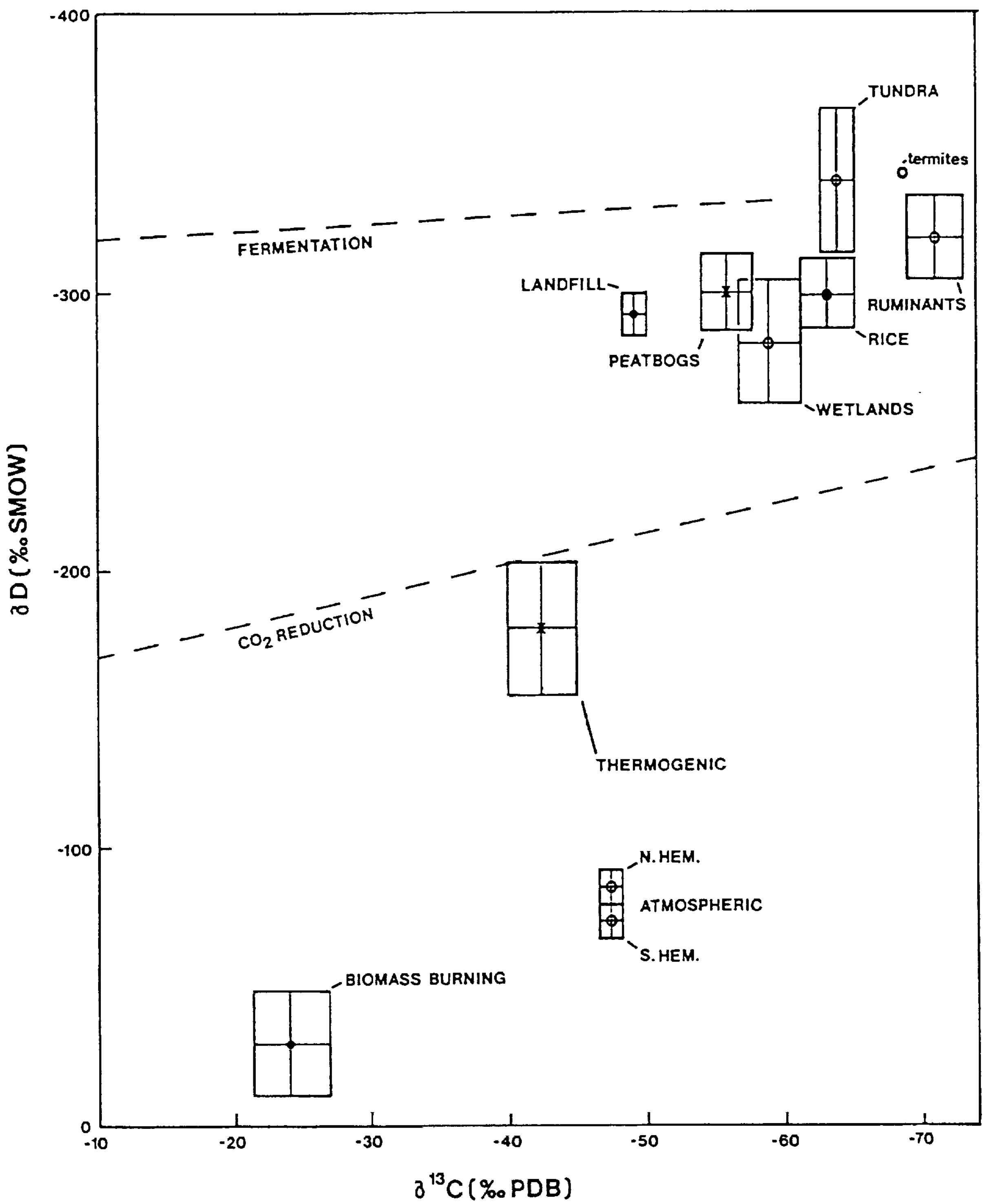
Figure 3. Chamber enclosure methane isotope values for selected 1994 and 1996 BOREAS samples as a function of log fraction of methane remaining. The scale is the same as for figure 1, as is the line α = 0.984. The line α = 0.988 is the fit of the 1996 NSA samples and the ambient air values.

Figure 4. The 1996 August and September NSA, BOREAS samples presented on an expanded scale and separated according to enclosure time. The lines shown are the regression fits and correlation values for the two time sets. The fractionation values (α) are given for each line.

Figure 5. Methane concentrations of BOREAS soil gas samples as a function of depth. Uncertainty in the depth determination may be 3-5 cm. Samples from the 1994 SSA are shown with a different symbol. The line represents a liner best fit of all the data.

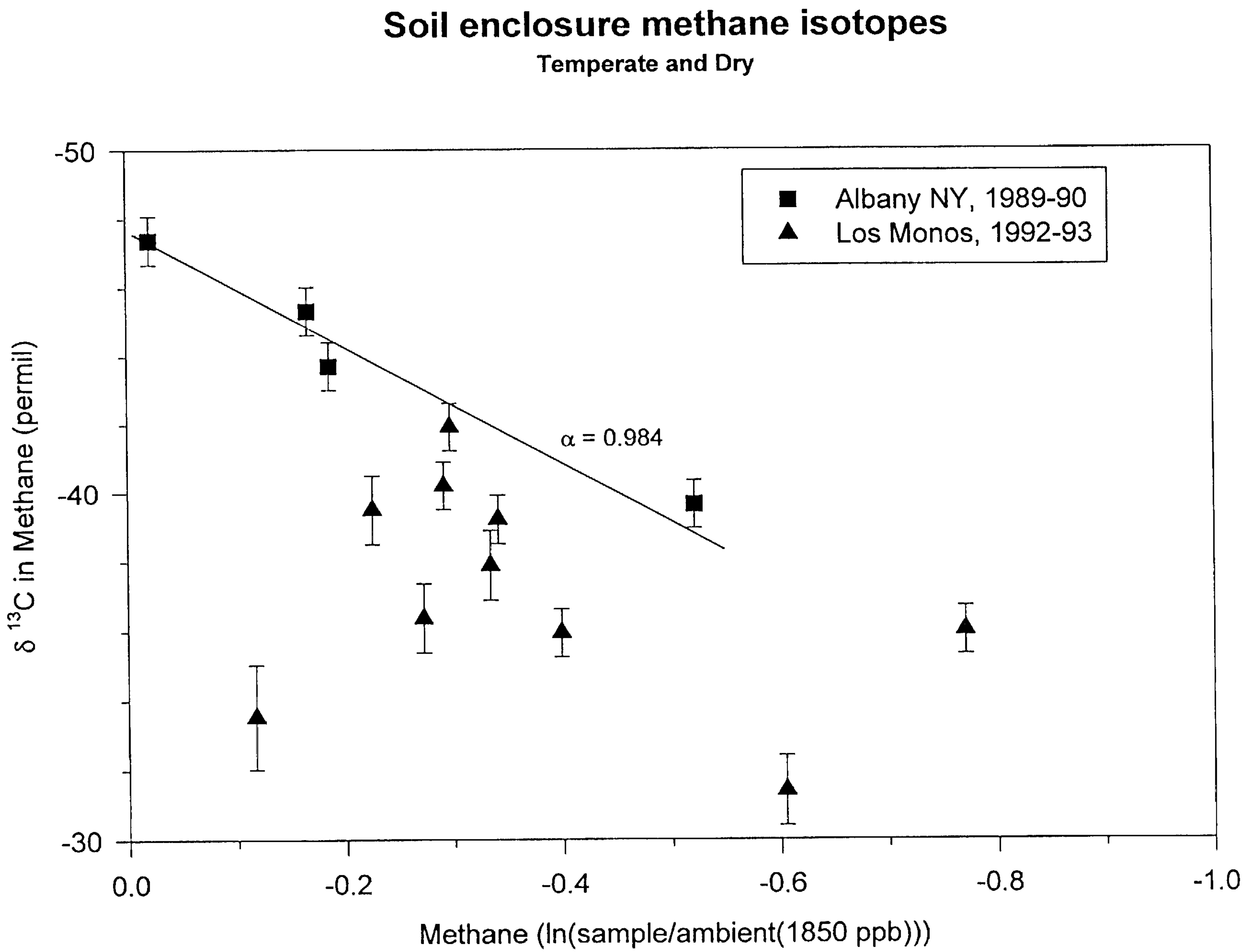
Figure 6. Methane Isotope values for the BOREAS soil gas samples as a function of depth. The symbols and regression are the same as in figure 5.

Figure 7. Methane isotope values in the BOREAS soil gas samples as a function of concentration, plotted as the natural log of the ratio of concentration to methane at 1850 ppb. The regression is a linear best fit with a slope yielding a hypothetical "α " of 0.9934.



TUNDRA
termites
FERMENTATION
LANDFILL
RUMINANTS
RICE
PEATBOGS
WETLANDS
CO_2 REDUCTION
THERMOGENIC
N. HEM.
ATMOSPHERIC
S. HEM.
BIOMASS BURNING
-400
-300
-200
-100
0
-10
-20
-30
-40
-50
-60
-70
δD (‰ SMOW)
$\delta^{13}C$ (‰ PDB)

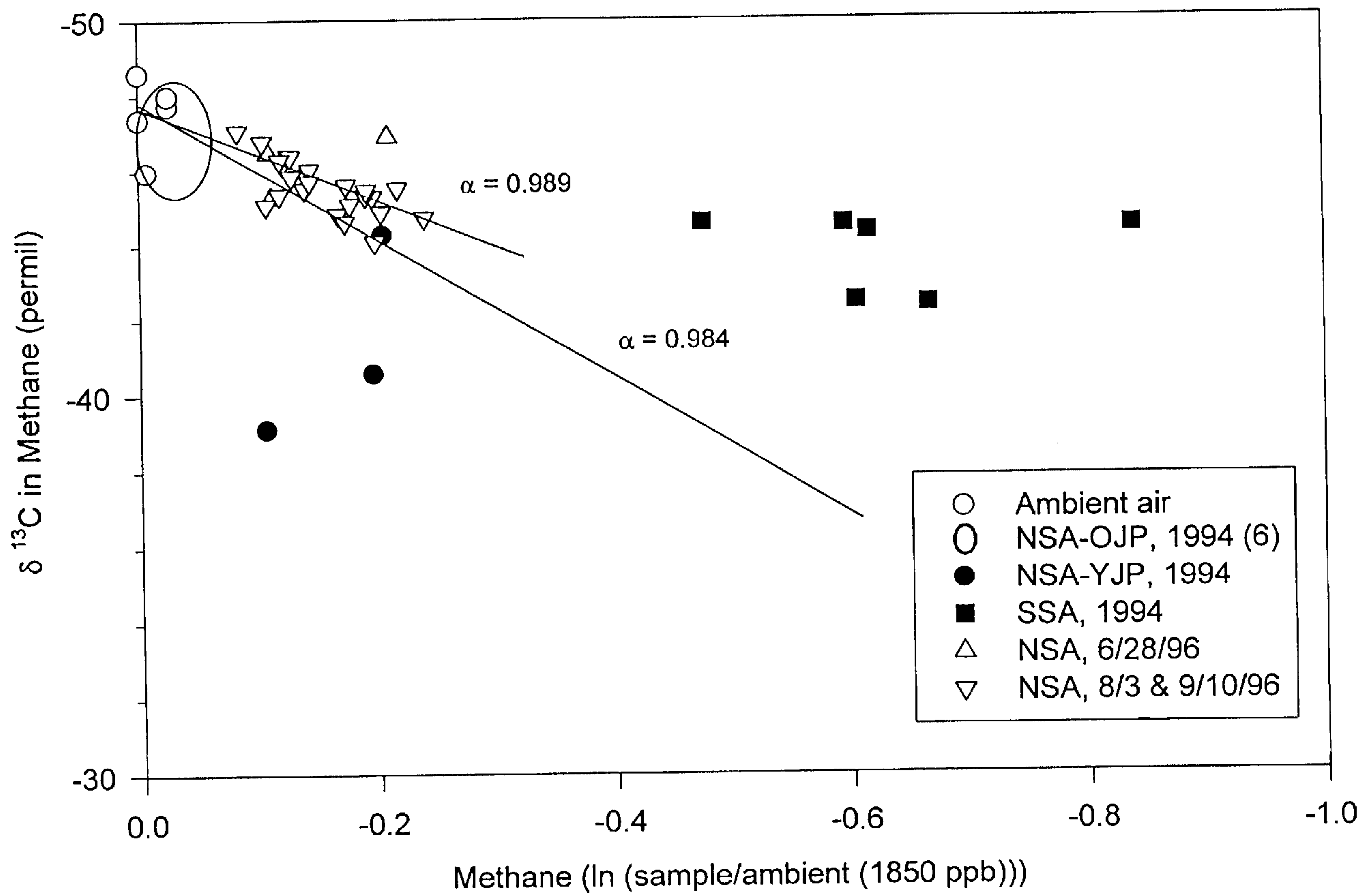
F·1


Soil enclosure methane isotopes
Temperate and Dry
-50
-40
-30
δ 13C in Methane (permil)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Methane (ln(sample/ambient(1850 ppb)))
Albany NY, 1989-90
Los Monos, 1992-93
α = 0.984

F2

Soil enclosure methane isotopes

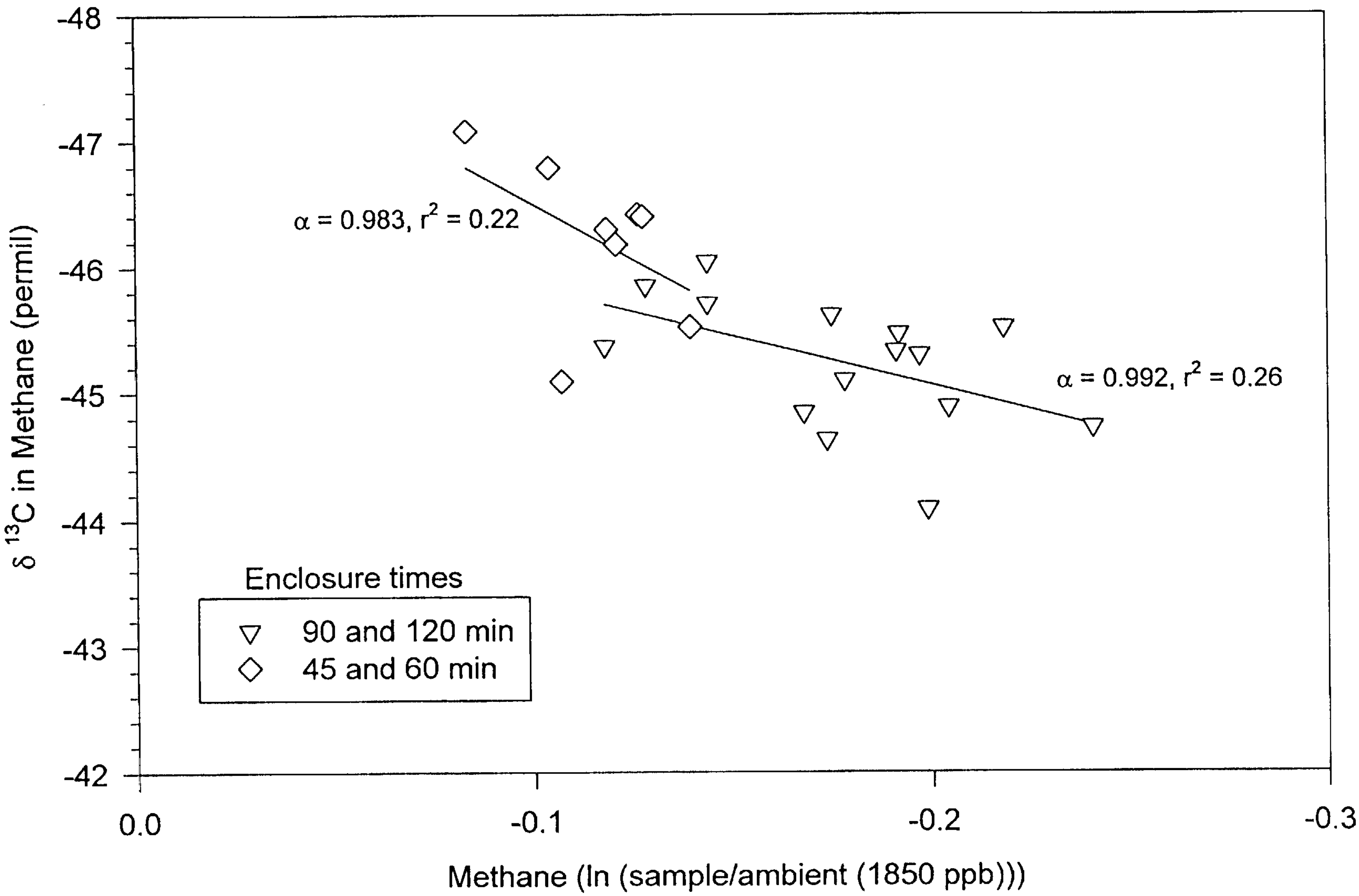
BOREAS Sites



F3

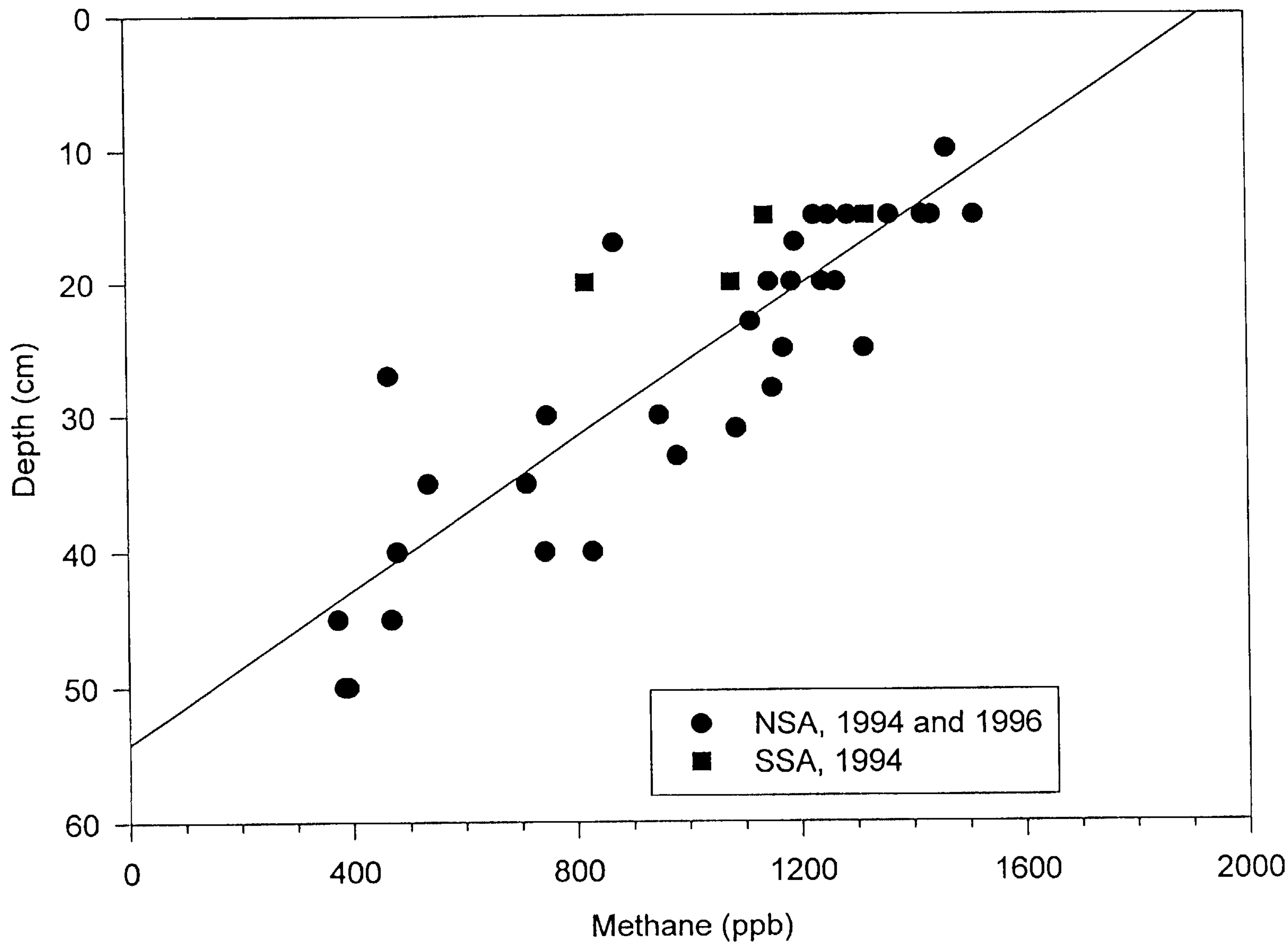
Soil enclosure methane isotopes

BOREAS Sites, Aug. & Sept. 1996



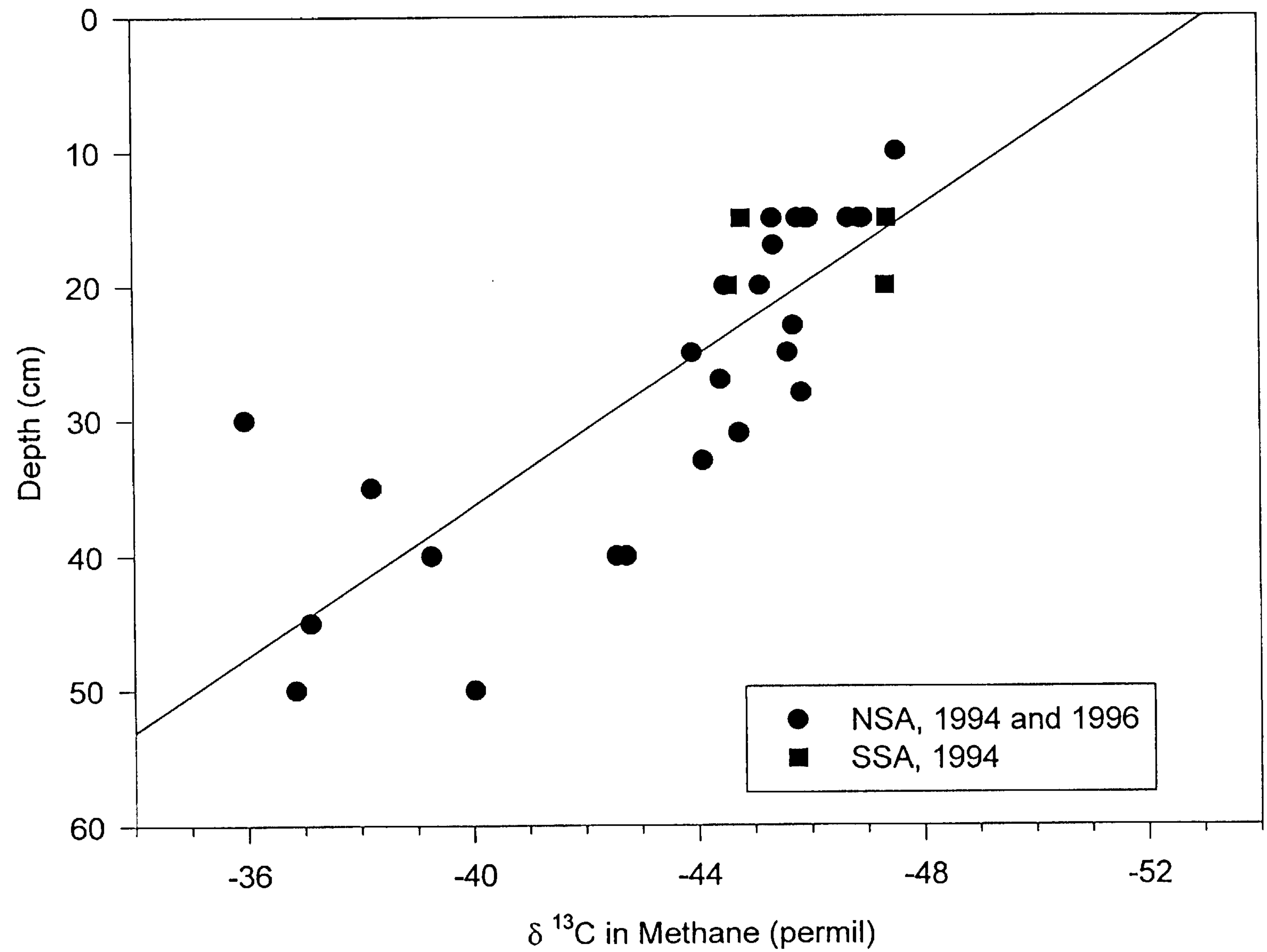
F4

Soil Methane Concentration

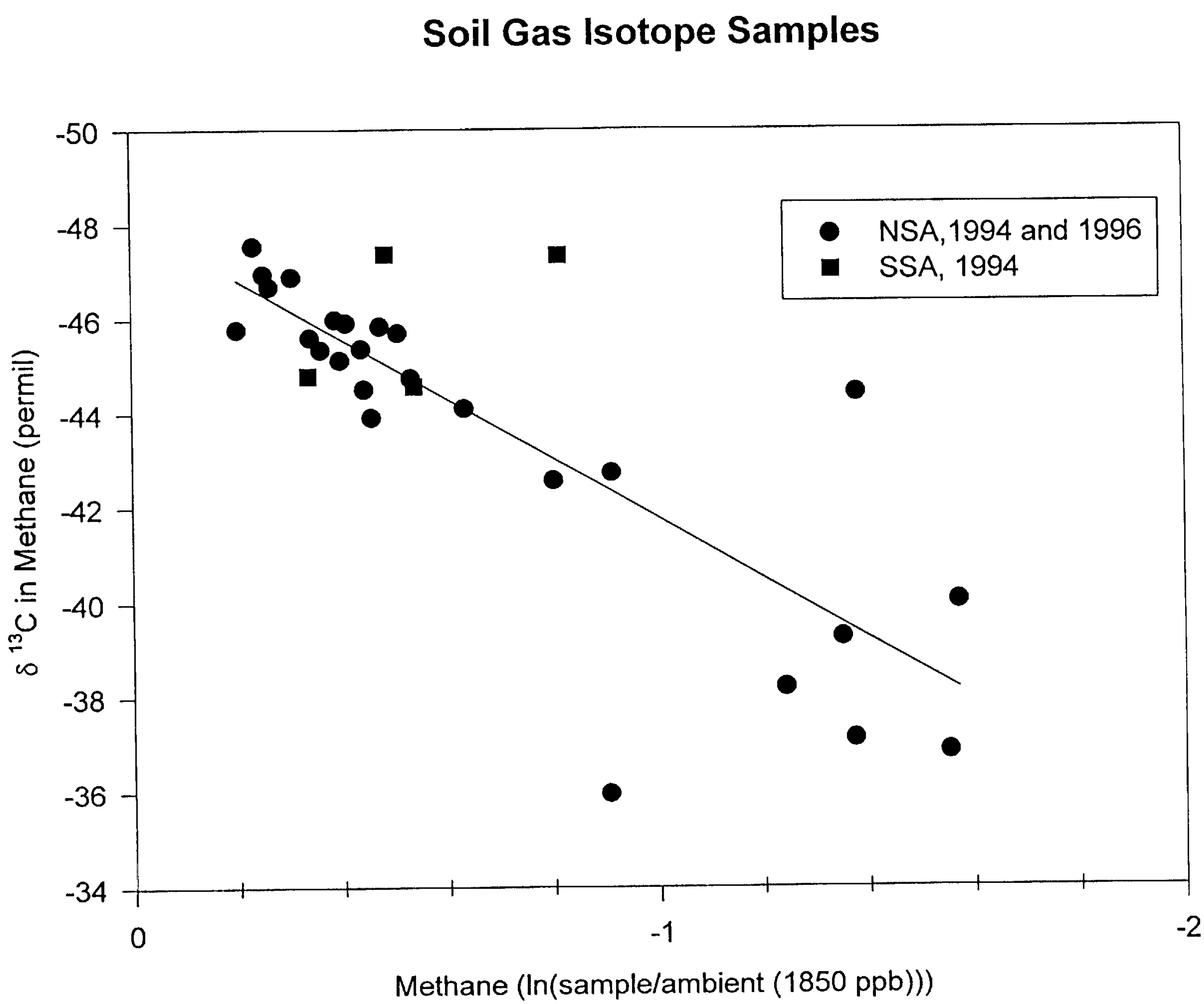


F5

Soil Methane Isotopes



F6


Soil Gas Isotope Samples
NSA,1994 and 1996
SSA, 1994
-50
-48
-46
-44
-42
-40
-38
-36
-34
δ 13C in Methane (permil)
0
-1
-2
Methane (ln(sample/ambient (1850 ppb)))

F7

Appendix 1
Methane samples from productions sites.

The data in this appendix is a combination of data from beaver pond and the Tower Fen sit taken in 1993 by gross bubble dislodgment into sampling funnels and in 1994 from several different sampling methods at the Tower Beaver Pond site.

For 1993, samples from the shore at the Gilliam road Beaver ponds, three beaver ponds near the Old Black Spruce tower site and the Tower Beaver Pond are presented with data from the Tower Fen site where the samples were taken from the walkways. Methane percentages in the dislodged bubbles ranged from less than 1% to greater than 60%. Samples taken at the Tower Beaver pond in 1993 had the highest average concentration of methane and, as shown on figure A1-1, had a ^{13}C composition heavier (less negative) than the average. The Gilliam Rd. Beaver pond had the lowest average % methane concentration, but the ^{13}C values for this site, as well as the other sites, had a wide range in values and were not remarkable when compared to each other. For the D/H data as a function of percent methane, the limited number of data points and the large range of values suggests the lack of a definite correlation. The exception to this may be the two Tower Fen data points which show the lightest (most negative) values. Few additional conclusions are justified given he spread in the data values and the limited number of data points from any one site.

The data from the multiple types of samples taken in 1994 at the Tower Beaver Pond suffer the same problems as the above samples, there are too few points for each sample type and the range in values is large.

The only conclusion that can be made viewing the results from the production sites is that the combination of production and oxidation in the sediments results in a large spread in the data values and that a correlation to the variables driving the production and oxidation must be made.

The data at the end of the appendix is presented in the same format as submitted to NASA for the BOREAS documentation set. A value of -9999 indicates a sample which due to error or lost in sampling or analysis is not reported.

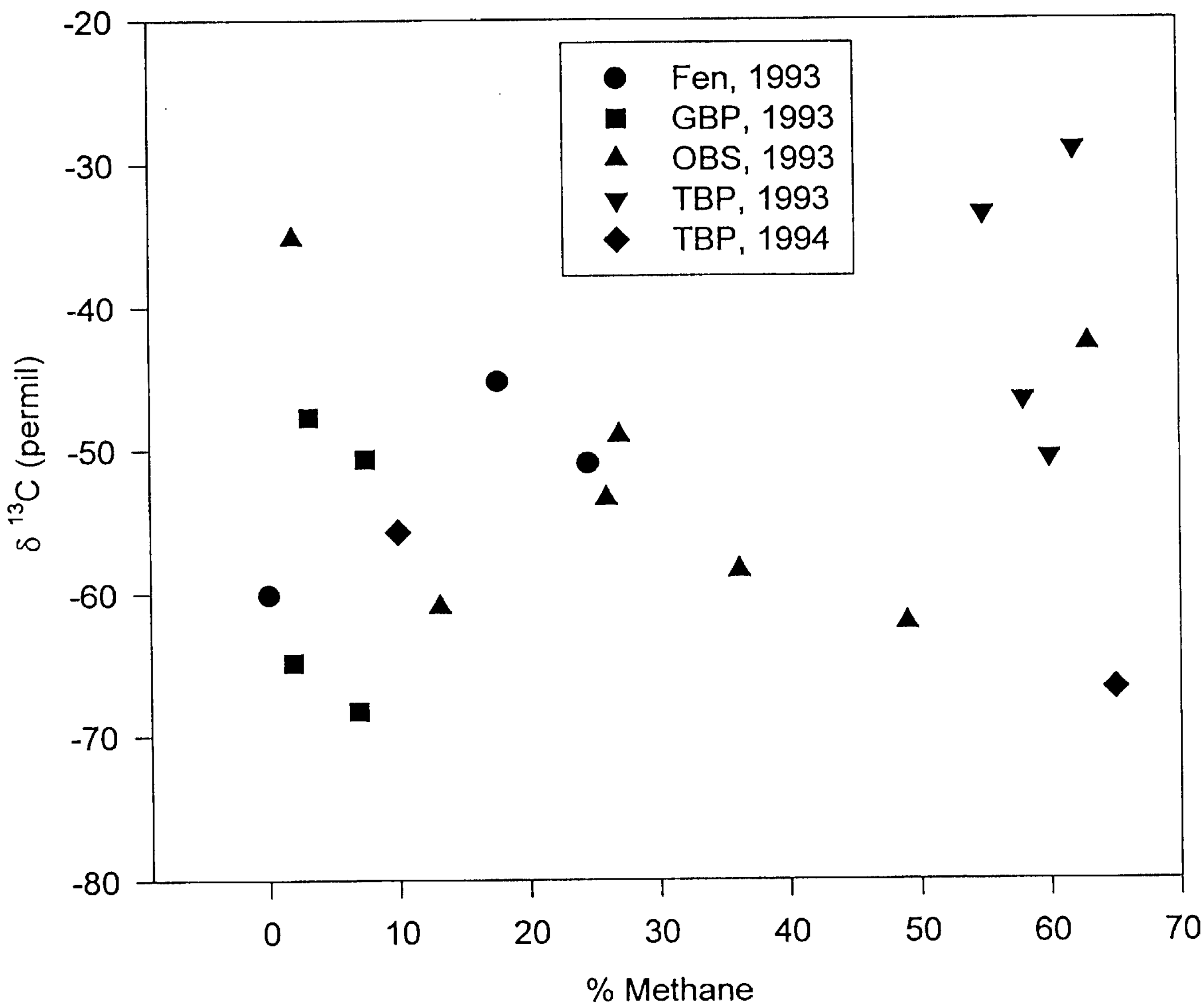
Figure A1-1. The ^{13}C isotopic composition in methane from the producing sites samples in 1993 and 1994 (NSA) as a function of percent methane in the dislodged bubbles. In order shown for legend: Tower Fen, Gilliam Road Beaver pond, Old Black Spruce beaver ponds, Tower Beaver Pond, 1993 and 1994.

Figure A1-2. The D/H isotopic composition in methane from dislodged bubbles as a function of percent methane. The legend is the same as in figure A1-1.

Figure A1-3. The isotopic values for methane from the production sites as a function of their D/H and ^{13}C composition. The legend is the same as in figure A1-1.

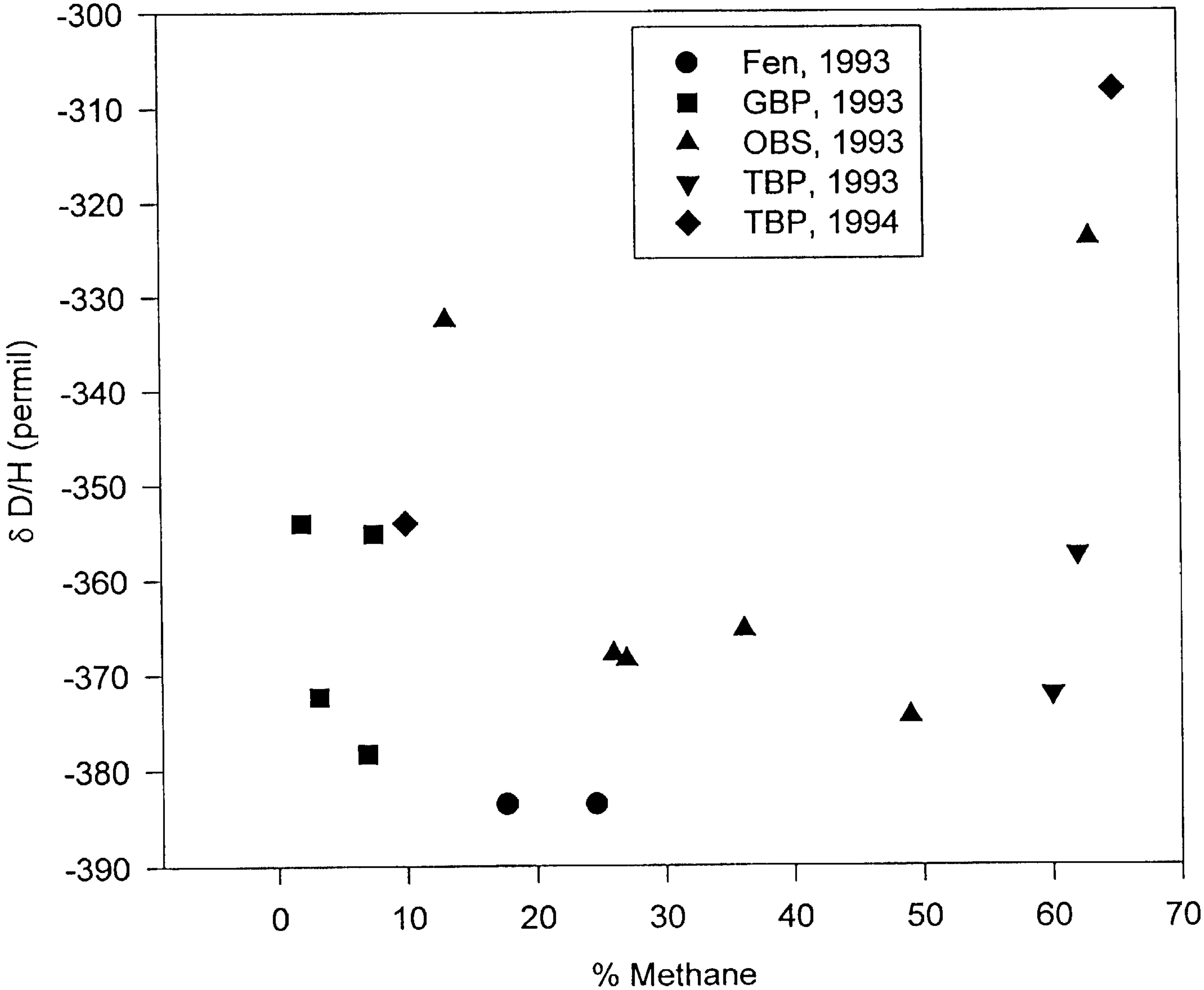
Figure A1-4. The isotopic composition, as functions of D/H and ^{13}C, for samples taken in 1993 and 1994 at the Tower Beaver Pond site in the NSA. Sample types shown in the legend were; dislodged bubbles; sub sediment pizometer water samples; water samples from immediately above the sediment; and funnel bubble collections at the water surface.

$\delta\ ^{13}C$ in Methane, Ponds and Fens

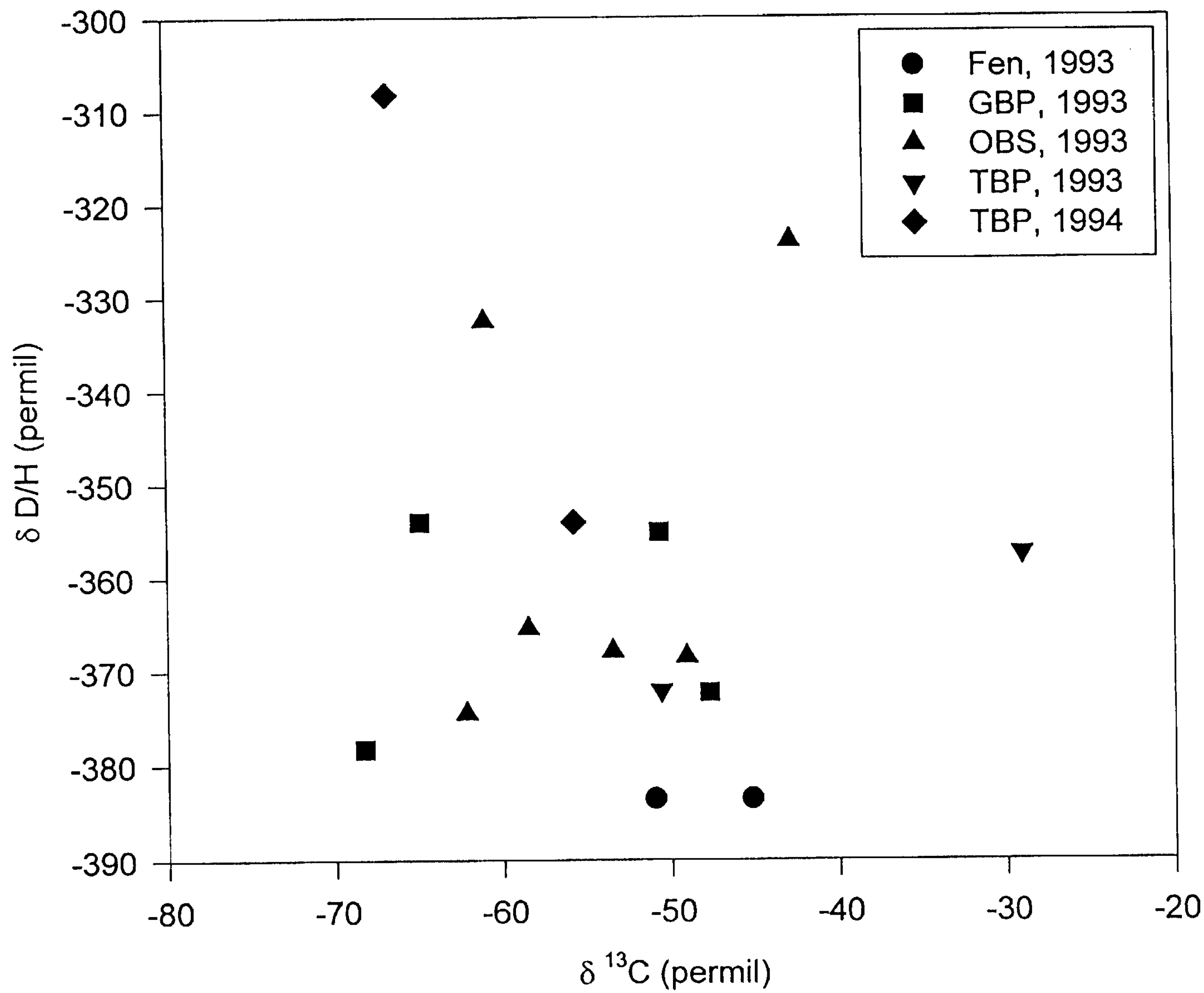


A1-1

D/H in Methane, Ponds and Fens

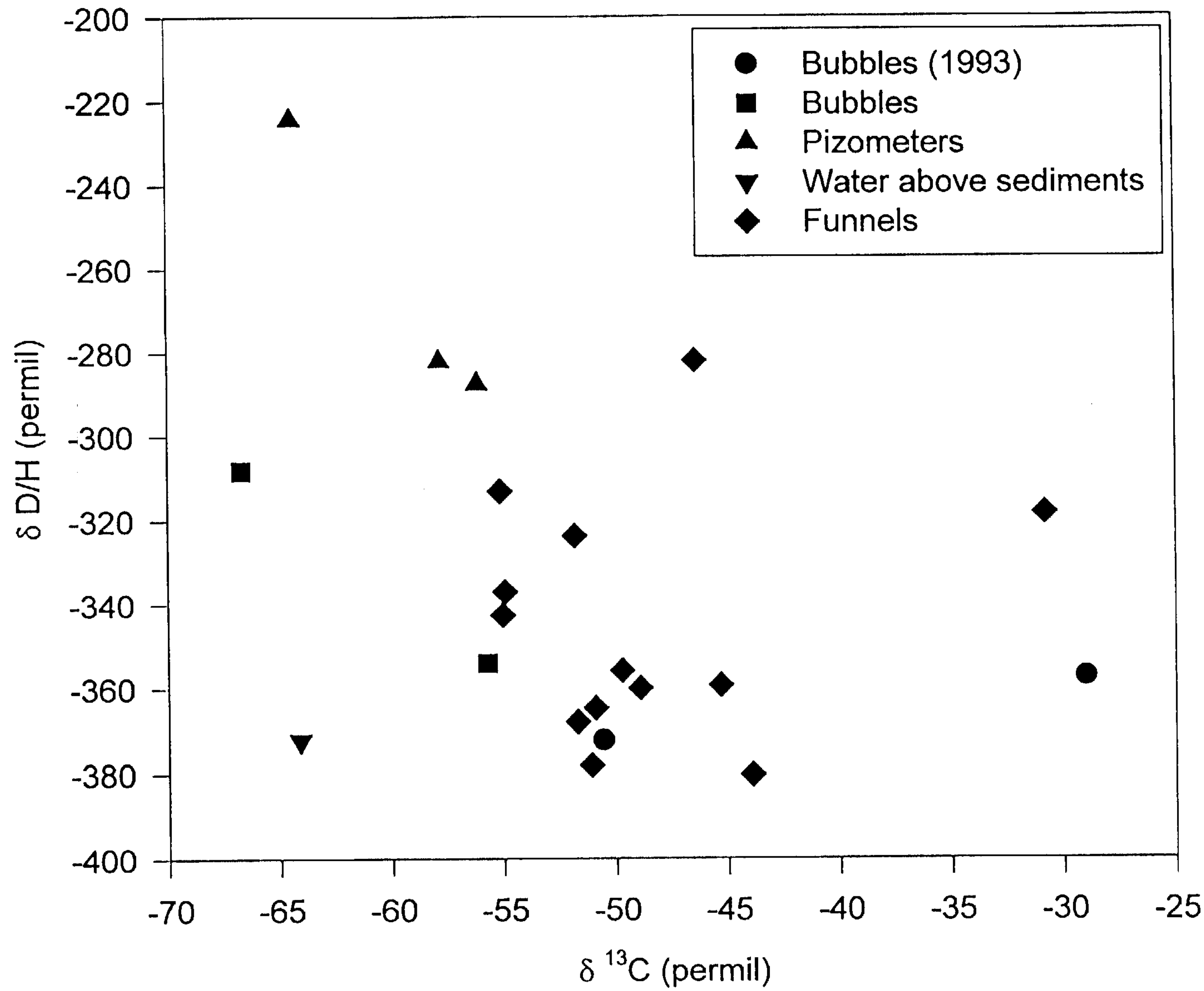


Methane Isotopes, Ponds and Fens



Methane Isotopes, Tower Bever Pond

By sample type



OBS_YEAI	OBS_DAY	S_TYPE	S_SITE	S_LOC	DEPTH	TIME	CH4_CON	C_ISO	D_ISO
YYYY	DD-MMM		0	0	0 Z cm	min.	%	permil	permil
1993	24-Aug	PB	NSA	TFEN x49	30	1	0.01	-9999	-9999
1993	24-Aug	PB	NSA	TFEN x45	30	1	0.01	-9999	-9999
1993	24-Aug	PB	NSA	TFEN x36	30	1	17.7	-45.2	-384
1993	24-Aug	PB	NSA	TFEN z46	30	1	0.01	-9999	-9999
1993	24-Aug	PB	NSA	TFEN z50	30	1	24.6	-51	-363
1993	24-Aug	PB	NSA	TFEN x1	30	1	0.02	-60.1	-9999
1993	25-Aug	PB	NSA	GBP z43	30	1	7.5	-50.7	-355
1993	25-Aug	PB	NSA	GBP b6	30	1	3.2	-47.7	-372
1993	25-Aug	PB	NSA	GBP x5	30	1	6.9	-68.3	-378
1993	25-Aug	PB	NSA	GBP z48	30	1	0.9	-9999	-9999
1993	25-Aug	PB	NSA	GBP b31	30	1	1.9	-64.9	-354
1993	26-Aug	PB	NSA	OBS 3 z49	30	1	13.2	-60.9	-333
1993	26-Aug	PB	NSA	OBS 3 x37	30	1	63	-42.7	-324
1993	26-Aug	PB	NSA	OBS 3 b301	30	1	49	-62.1	-375
1993	26-Aug	PB	NSA	OBS 4 z41	30	1	2	-35.2	-9999
1993	26-Aug	PB	NSA	OBS 4 x28	30	1	36.2	-58.5	-365
1993	26-Aug	PB	NSA	OBS 1 x26	30	1	26	-53.5	-368
1993	26-Aug	PB	NSA	OBS 1 x21	30	1	27	-49.1	-367
1993	26-Aug	PB	NSA	TBP x11	30	1	55	-33.5	-9999
1993	26-Aug	PB	NSA	TBP z42	30	1	58	-46.5	-9999
1993	26-Aug	PB	NSA	TBP z44	30	1	62	-39	-357
1993	26-Aug	PB	NSA	TBP b339	30	1	60	-50.6	-372
1994	25-Aug	F	NSA	TBP 92	30	1	2.7	-51.8	-324
1994	25-Aug	F	NSA	TBP 88	0	1	10.7	-51.1	-378
1994	25-Aug	F	NSA	TBP 96	0	1	24.2	-51.7	-368
1994	25-Aug	F	NSA	TBP 99	0	1	18.9	-49.7	-356
1994	25-Aug	F	NSA	TBP 101	0	1	17.3	-43.9	-380
1994	25-Aug	F	NSA	TBP 105	0	1	15.4	-45.3	-359
1994	25-Aug	F	NSA	TBP 109	0	1	6.4	-30.8	-318
1994	25-Aug	F	NSA	TBP 114	0	1	6.7	-46.4	-282
1994	25-Aug	PZ	NSA	TBP a	100	1	0.01	-9999	-9999
1994	25-Aug	PZ	NSA	TBP b	60	1	0.03	-9999	-9999

1994	25-Aug PZ	NSA	TBP c	50	1	0.7	-56.1	-288
1994	25-Aug PZ	NSA	TBP d	30	1	0.19	-43	-9999
1994	25-Aug PZ	NSA	TBP e	10	1	0.11	-54	-9999
1994	25-Aug PZ	NSA	TBP l	70	1	0.02	-9999	-9999
1994	25-Aug PZ	NSA	TBP n	30	1	1.1	-9999	-9999
1994	25-Aug WC	NSA	TBP 72	2	1	1.24	-64.1	-372
1994	25-Aug WC	NSA	TBP 76	10	1	1.06	-64.2	-9999
1994	31-Aug PB	NSA	TBP 89	30	1	65	-66.7	-308
1994	1-Sep F	NSA	TBP 87 f3	0	1	29	-50.9	-365
1994	1-Sep F	NSA	TBP 91 f13	0	1	-9999	-9999	-9999
1994	1-Sep F	NSA	TBP 96 f23	0	1	10.2	-48.9	-360
1994	1-Sep F	NSA	TBP 94 f29	0	1	3.4	-55	-343
1994	1-Sep F	NSA	TBP 103 f36	0	1	55.4	-54.9	-337
1994	1-Sep F	NSA	TBP 106 f1	0	1	2.7	-55.1	-313
1994	13-Sep WC	NSA	TBP 11	0	1	0.97	-9999	-9999
1994	13-Sep WC	NSA	TBP 25	10	1	0.1	-32	-9999
1994	13-Sep PZ	NSA	TBP a	100	1	0.66	-66.7	-9999
1994	13-Sep PZ	NSA	TBP b	70	1	0.53	-64.4	-224
1994	13-Sep PZ	NSA	TBP c	50	1	1.22	-58.1	-9999
1994	13-Sep PZ	NSA	TBP d	30	1	0.7	-57.8	-282
1994	13-Sep PZ	NSA	TBP e	10	1	0.25	-60.2	-9999
1994	13-Sep PZ	NSA	TBP m	50	1	0.64	-65.7	-9999
1994	13-Sep PZ	NSA	TBP o	10	1	1.9	-31.9	-9999
1994	13-Sep PB	NSA	TBP 116	30	1	10	-55.7	-354

Appendix 2

Data from the Chamber Enclosures and Soil Gas samples

CHECSV are the chamber enclosure results. C_ISO values are ^{13}C in permil. The data is formatted as reported for the documentation set. -9999 indicates a sample lost or not reported.

SPECSV are the results of the soil gas measurements.

OBS_YEAI	OBS_DAY	S_TYPE	S_SITE	S_LOC	DEPTH	TIME	CH4_CON	C_ISO
YYYY	DD-MMM	0	0	0	Z cm	min	ppbv	permil
1994	4-Aug	C	SSA	YJP A	0	825	1150	-44.6
1994	4-Aug	C	SSA	YJP B	0	825	1000	-44.4
1994	4-Aug	C	SSA	YJP D	0	825	950	-42.4
1994	4-Aug	C	SSA	OJP G	0	960	1010	-42.5
1994	4-Aug	C	SSA	OJP H	0	960	1020	-44.6
1994	4-Aug	C	SSA	OJP J	0	960	800	-44.5
1994	24-Aug	C	NSA	OJP #4-1	0	82	1838	-46.1
1994	24-Aug	C	NSA	OJP #4-1	0	147	1798	-46.7
1994	24-Aug	C	NSA	OJP #4-2	0	60	1830	-47.7
1994	24-Aug	C	NSA	OJP #4-2	0	120	1798	-46.6
1994	24-Aug	C	NSA	OJP #4-3	0	60	1742	-47
1994	24-Aug	C	NSA	OJP #4-3	0	96	1734	-48.5
1994	24-Aug	C	NSA	YJP #4-4	0	61	1520	-40.6
1994	24-Aug	C	NSA	YJP #4-5	0	62	1665	-39.1
1994	24-Aug	C	NSA	YJP #4-6	0	64	1507	-44.3
1996	3-Jun	C	NSA	OJP #4	0	260	1524	-42.4
1996	3-Jun	C	NSA	OJP #7	0	270	1567	-37.6
1996	3-Jun	C	NSA	YJP #4	0	400	1583	-52
1996	3-Jun	C	NSA	YJP #6	0	410	1502	-43.1
1996	28-Jun	C	NSA	OJP #4	0	110	1659	-46.5
1996	28-Jun	C	NSA	OJP #7	0	120	1613	-45.8
1996	28-Jun	C	NSA	YJP #4	0	80	1499	-46.9
1996	28-Jun	C	NSA	YJP #6	0	75	1655	-45.3
1996	2-Aug	C	NSA	OJP #4	0	45	1630	-46.4
1996	2-Aug	C	NSA	OJP #4	0	90	1564	-44.8
1996	2-Aug	C	NSA	OJP #4	0	92	1553	-45.6
1996	2-Aug	C	NSA	OJP #7	0	45	1609	-45.5
1996	2-Aug	C	NSA	OJP #7	0	90	1454	-44.7
1996	2-Aug	C	NSA	OJP #7	0	92	1454	-9999
1996	3-Aug	C	NSA	YJP #6	0	60	1639	-46.2
1996	3-Aug	C	NSA	YJP #6	0	119	1519	-45.3
1996	3-Aug	C	NSA	YJP #6	0	121	1508	-44.9
1996	3-Aug	C	NSA	YJP #4	0	61	1702	-47.1
1996	3-Aug	C	NSA	YJP #4	0	120	1627	-45.9
1996	3-Aug	C	NSA	YJP #4	0	122	1602	-46
1996	8-Sep	C	NSA	YJP #4	0	61	1628	-46.4
1996	8-Sep	C	NSA	YJP #4	0	120	1516	-44.1
1996	8-Sep	C	NSA	YJP #4	0	122	1487	-45.5
1996	8-Sep	C	NSA	YJP #6	0	60	1667	-46.8
1996	8-Sep	C	NSA	YJP #6	0	121	1602	-45.7
1996	8-Sep	C	NSA	YJP #6	0	123	1644	-45.4
1996	11-Sep	C	NSA	OJP #4	0	60	1662	-45.1
1996	11-Sep	C	NSA	OJP #4	0	120	1555	-44.6
1996	11-Sep	C	NSA	OJP #4	0	122	1548	-45.1
1996	11-Sep	C	NSA	OJP #7	0	60	1643	-46.3
1996	11-Sep	C	NSA	OJP #7	0	120	1528	-45.3
1996	11-Sep	C	NSA	OJP #7	0	122	1527	-45.5

1996	24-Aug	A	NSA	OJP	0	0	1880	-9999
1996	24-Aug	A	NSA	YJP	0	0	1850	-48.6
1996	24-Aug	A	NSA	YJP	0	0	1856	-47.4
1996	26-Aug	A	NSA	YJP	0	0	1840	-9999
1996	11-Sep	A	NSA	YJP	0	0	1805	-47.8
1996	11-Sep	A	NSA	YJP	0	0	1805	-48

OBS_YEAI	OBS_DAY	S_TYPE	S_SITE	S_LOC	DEPTH	TIME	CH4_CON	C_ISO
YYYY	DD-MMM	0	0	0	Z cm	min	ppbv	permil
1994	4-Aug	S	SSA	YJP A/B	15	1	1140	-47.4
1994	4-Aug	S	SSA	YJP A/B	20	1	820	-47.4
1994	4-Aug	S	SSA	OJP G/H	15	1	1320	-44.8
1994	4-Aug	S	SSA	OJP G/H	20	1	1080	-44.6
1994	24-Aug	S	NSA	OJP #4-1	35	1	535	-38.2
1994	24-Aug	S	NSA	OJP #4-1.1	45	1	374	-9999
1994	24-Aug	S	NSA	OJP #4-2	50	1	392	-36.3
1994	24-Aug	S	NSA	OJP #4-2.2	40	1	480	-39.3
1994	24-Aug	S	NSA	OJP #4-3	35	1	712	-9999
1994	24-Aug	S	NSA	OJP #4-3.1	50	1	385	-40
1994	24-Aug	S	NSA	OJP #4-3.2	30	1	950	-9999
1994	24-Aug	S	NSA	YJP #4-4	45	1	469	-37.1
1994	24-Aug	S	NSA	YJP #4-4.1	30	1	749	-36
1994	24-Aug	S	NSA	YJP #6-5	20	1	1267	-9999
1994	24-Aug	S	NSA	YJP 6	28	1	1152	-45.9
1994	24-Aug	S	NSA	YJP 6.1	33	1	982	-44.1
1994	24-Aug	S	NSA	YJP 6.2	31	1	1087	-44.8
1994	26-Aug	S	NSA	YJP 1c	40	1	744	-42.7
1994	26-Aug	S	NSA	YJP 3a	40	1	830	-42.5
1994	26-Aug	S	NSA	YJP 1c	20	1	1188	-44.6
1994	26-Aug	S	NSA	YJP 3a	20	1	1147	-9999
1996	2-Aug	S	NSA	YJP #4-1	15	1	1513	-45.8
1996	2-Aug	S	NSA	YJP #4-2	27	1	466	-44.4
1996	2-Aug	S	NSA	YJP #7-3	15	1	1254	-46
1996	2-Aug	S	NSA	YJP #7-4	20	1	1243	-45.1
1996	3-Aug	S	NSA	YJP #6-1	25	1	1316	-45.6
1996	3-Aug	S	NSA	YJP #6-2	15	1	1362	-46.9
1996	3-Aug	S	NSA	YJP #4-3	15	1	1422	-46.7
1996	3-Aug	S	NSA	YJP #4-4	23	1	1114	-45.7
1996	8-Sep	S	NSA	YJP #6-1	17	1	1194	-45.4
1996	8-Sep	S	NSA	YJP #6-2	15	1	1229	-45.9
1996	8-Sep	S	NSA	YJP #4-3	10	1	1465	-47.6
1996	8-Sep	S	NSA	YJP #4-4	15	1	1289	-45.4
1996	11-Sep	S	NSA	OJP #4-1	15	1	1437	-47
1996	11-Sep	S	NSA	OJP #7-2	17	1	871	-9999